Regioselective S—O vs. C—O bond cleavage in sulfenate ester radical anions¹

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Abstract: The electron transfer (ET) reduction of benzyl benzenesulfenate ester (1) and *tert*-butyl benzenesulfenate ester (2) was investigated using electrochemical techniques. Analysis of the cyclic voltammetry of each compound suggests that the ET reduction proceeds via a stepwise dissociative mechanism. The voltammograms of 1 are similar to those of diaryl disulfides and it was found through controlled potential electrolysis (CPE) product studies that ET reduction leads to S—O bond cleavage. The voltammograms of 2 are dramatically different with a sharper dissociative wave occurring at a more negative peak potential. CPE experiments indicate products that result from ET leading to C—O bond cleavage in this case. DFT calculations of the singly occupied molecular orbitals (SOMOs) of 1 and 2 were performed and offer a rationale for the different reactivity of the two radical anions.

Key words: sulfenate esters, dissociative electron transfer, electrochemistry, radical anions.

Résumé : On a étudié la réaction de réduction par transfert d'électron (TE) du benzènesulfénate de benzyle (1) et du benzènesulfénate de *tert*-butyle (2) en faisant appel à des techniques électrochimiques. L'analyse de la voltampérométrie cyclique de chaque composé suggère que la réduction par TE se produit par un mécanisme par dissociations successives. Le voltampérogramme du composé 1 est semblable à celui des disulfures de diaryles et, sur la base d'études des produits par électrolyse à potentiel contrôlé (EPC), on a trouvé que la réduction par TE conduit à une coupure de la liaison S—O. Le voltampérogramme du composé 2 est dramatiquement différent et il présente une vague dissociative qui se présente à un pic de potentiel beaucoup plus négatif. Les études d'EPC indiquent que, dans ce cas, les produits qui résultent d'un TE proviennent d'une coupure d'une liaison C—O. Des calculs effectués sur la base de la théorie de la densité fonctionnelle des orbitales moléculaires à occupation singulet (SOMO) des composés 1 et 2 et ils permettent de présenter une rationalisation pour les réactivités différentes des deux radicaux anions.

Mots clés : esters de l'acide sulfénique, transfert d'électron avec dissociation, électrochimie, radicaux anions.

[Traduit par la Rédaction]

Introduction

A major focus of our group has been the study of dissociative electron transfer (ET) reactions through electrochemical methods. The work provides an opportunity to investigate many aspects of ET reactions, but also allows for investigation into the reactivity of the intermediate species formed upon ET. Studies of 9,10-diphenylanthracene endoperoxide found that upon ET reduction, O—O bond cleavage occurred generating an alkoxyl radical (1, 2). It was observed that an O-neophyl type rearrangement at the alkoxyl radical could occur in competition with its ET reduction. Similarly, the dissociative ET reduction of 3,3,6,6tetraaryl-1,2-dioxanes involved formation of a distonic radical anion (where the radical and anionic centres are spatially and electronically distinct), which could be reduced or could

Received 27 April 2005. Published on the NRC Research Press Web site at http://canjchem.nrc.ca on 10 November 2005.

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¹This article is part of a Special Issue dedicatted to organic reaction mechanisms.

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fragment (3). The fragmentation pathway led to a homogeneous ET-fragmentation radical anion chain reaction that was responsible for a potential dependence on the product ratios of controlled potential electrolysis (CPE) experiments. Both cases demonstrate the unique reactivity that can be observed upon generation of radical anion species by electrochemical means, and how the reactivity can be controlled by adjusting the potential at which they are formed. In this sense, the electrochemical generation of radical anions makes for ideal circumstances to investigate their reactivity.

The study of sulfenate esters developed as an extension to our work on the ET reduction of peroxides (4-7) and endoperoxides (1-3, 8-10) and the work of others concerning the ET reduction of diaryl disulfides (11–14). The ET reduction of the O-O bonds in peroxides and endoperoxides and the S-S bonds in diaryl disulfides are characterized by unusually large values for the intrinsic barrier for the ET (ΔG_0^{\ddagger}). For the ET reduction of peroxides and endoperoxides the ET is shown to cleave the O-O bond via a concerted dissociative mechanism where electron uptake and bond cleavage are simultaneous. In this case, the large intrinsic barrier is a result of a contribution from the bond dissociation energy of the fragmenting bond. In contrast, the reduction of diaryl disulfides was shown to follow a stepwise dissociative mechanism, with the formation of a radical anion intermediate that leads to fragmentation of the S-S bond in a second

Parameters	Scan rates (V/s)	1	$1 + acid/MeOTs^{a}$	2	$2 + \operatorname{acid}^{b}$
$\overline{E_{p}}$ (V vs. SCE)	0.1	-1.68	-1.67	-2.28	-2.29
1	1.0	-1.76	-1.75	-2.36	-2.35
	10.0	-1.89	-1.89	-2.48	-2.43
$\Delta = (E_{\rm p/2} - E_{\rm p}) \ (\rm mV)$	0.1	117	96	83	86
	1.0	124	91	95	96
	10.0	156	127	129	110
$I_p / v^{1/2} (mA s^{1/2} V^{-1/2})^c$		107	164	144	170
$\alpha = 1.85 \frac{RT}{F} \Delta$	0.1	0.41	0.50	0.58	0.60
	1.0	0.38	0.52	0.50	0.55
		0.31	0.37	0.37	0.49
$\alpha_{\rm app} = \frac{RT}{nF} \left(\frac{\partial \ln v}{\partial E_{\rm p}} \right)$		0.35	0.38	0.28	0.41
$\partial E_{\rm p}/\partial \log v ({\rm mV})$		-83	-78	-103	-72
$n = Q/mF \ (F/mol)^d$		1.1	1.9	1.1	2.0

Table 1. Data obtained from the CVs of 1 and 2 (1.0-3.0 mmol/L) in 0.1 mol/L TBAP-DMF solution.

^{*a*}Average of multiple experiments where either acetanilide or TFE was used in at least two times excess in combination with at least 1 equiv. of MeOTs.

^bCVs preformed in the presence of at least a two times excess of acetanilide.

^cCorrected for a 2 mmol/L solution.

^{*d*}Equation determines the stoichiometry of an electroysis based on the charge introduced into the cell (Q), the mol of analyte (m), and Faraday constant.

Scheme 1.



step. For the disulfides, the large intrinsic barrier was shown to be the result of contributions due to a significant S—S bond stretching upon ET forming a loosely bound radical anion intermediate. To further examine the factors that govern the stepwise vs. concerted mechanism in these types of bonded systems, we initiated this study of the ET to sulfenate esters, which contain a single S—O bond.

Although isoelectronic with peroxides (O-O) and disulfides (S-S), the S-O bonded sulfenate esters might reasonably be expected to show some differences in reactivity because the relative size and electronegativity of the two atoms in the bond are different. Because the chemistry of a compound initiated by ET and photochemical excitation often follow similar pathways, then it is constructive to note that in the many investigations of the photochemistry of sulfenate esters it is uniformly demonstrated that S-O bond cleavage occurs upon excitation (15, 16), similar to both peroxides and disulfides that undergo photolytic O-O and S-S cleavage, respectively. This offers reason to suspect that upon ET reduction these compounds would then undergo S-O cleavage as well. However, a computational study by Gregory and Jenks (17) suggests that compared to R-O-O-R' peroxides, sulfenic esters (R-S-O-R') can have much weaker R'-O bonds than the stronger central S-O or the corresponding R-S bonds. This suggests that sulfenic esters may indeed exhibit different reactivity compared to peroxides and disulfides. In this study the ET reduction of benzyl benzenesulfenate ester (1) and *tert*-butyl benzenesulfenate ester (2), shown in Scheme 1, was examined. These substrates vary only in the ester functionality, which is ideal for probing the impact of this group on the reactivity. Both substrates are derivatives of benzenesulfenic acid, which provides a convenient handle for comparison to diaryl disulfides. The work reported here details the analysis of the cyclic voltammetry (CV) and the CPE for each compound to determine the mechanism of the initial ET and investigate the reactivity of any radical anion species formed through ET reduction.

Results and discussion

ET reduction of benzyl benzenesulfenate ester (1)

The cyclic voltammetry of 1 was performed in dimethylformamide (DMF) with 0.1 mol/L tetrabutylammonium perchlorate (TBAP) as supporting electrolyte. The pertinent CV data for both 1 and 2 are listed in Table 1. A representative CV of 1 in the absence of acid is shown in Fig. 1*a*. When scanning cathodically, a broad wave with low peak current is observed at -1.68 V vs. SCE at 0.1 V/s, which is assigned as the dissociative wave of 1. This wave is irreversible at all scan rates investigated (0.1-50.0 V/s). The peak current corrected for scan rate and concentration is 107 µA for a 2 mmol/L solution. The peak current provides an indication of the number of electrons involved in the reduction step. The $E_{\rm p}$ shifts negatively with increasing scan rate by 83 mV/decade. The peak breadth also increases, from values of 117 to 124 mV at 0.1 and 1.0 V/s, respectively, which leads to the corresponding decrease in the transfer coefficient (α), with values of 0.41 and 0.38 at the same scan

Fig. 1. Representative CVs of **1** in 0.1 mol/L TBAP–DMF at 0.1 V/s: (*a*) **1** (2.3 mmol/L) before (solid line) and after (dashed line) introduction of 6.1 C of charge into the cell; (*b*) **1** (2.2 mmol/L) in the presence of acetanilide (40 mmol/L) and MeOTs (40 mmol/L) before (solid line) and after (dashed line) introduction of 10.3 C of charge into the cell.



rates. A shoulder is present on the tail of this wave and following this is another small wave that appears to be quasireversible. Both of the latter two features are present due to the reduction of products formed from parent-child reactions, where 1 (the parent) reacts with a basic or nucleophilic anionic species (the child) generated from the ET reduction of 1. Reversing to scan anodically, a large oxidation near 0 V vs. SCE is observed and is attributed primarily to the oxidation of phenylthiolate (3) to the phenylthiyl radical (18). Because of the similarity in oxidation potentials, this wave may also include the oxidation of phenylmethoxide anion (4), and at slower scan rates this wave does appear to be composed of two overlapping oxidation peaks. The presence of 3 is confirmed by reversing the scan direction to scan cathodically following this large oxidation peak. A reduction wave attributable to diphenyl disulfide is observed, though this wave is exceedingly broad because of fouling of the working electrode by the putative phenylthiyl radicals. The analysis of the CVs indicates that the ET reduction occurs by the mechanism shown in Scheme 2. The initial ET occurs to form a radical anion intermediate, which then cleaves at the S-O bond in a separate step. The cleavage of the radical anion generates phenylthiolate (3) and the phenylmethoxyl radical. The alter-

Scheme 2. Proposed mechanism for the ET reduction of 1.



nate mode of cleavage (phenylthiyl radical and phenylmethoxide anion) is less favoured as the phenylthiyl radical is estimated to have a more negative reduction potential than the phenylmethoxyl radical (18). Regardless of the mode of cleavage, the reduction potential of the radical formed is far positive of the reduction potential of **1** and undergoes a rapid ET to give the phenylmethoxide anion (**4**).

The reduction waves following the dissociative wave of **1** are due to products from the reactions involving the anionic species **3** or **4** reacting with **1** or the medium. The addition of an acid, such as acetanilide or 2,2,2-trifluoroethanol (TFE), will result in the protonation of **4**, eliminating any reactions of this anion with **1**. The pK_{as} of benzenethiol, acetanilide, and TFE as determined in DMSO are 10.3, 21.45, and 23.45, respectively (19). Given the relative pK_{a} values for these compounds, it is apparent why acetanilide and TFE have a limited capacity to protonate **3**. Therefore, the addition of these acids does not hinder the ability of **3** to react with **1**, even when present in large excess. In this case, to trap any **3** produced in the reduction of **1** a nucleophile trap such as methyl *p*-toluenesulfonate (MeOTs) or methyl iodide (MeI) is added.

The addition of both an acid and nucleophile trap is necessary to observe the full peak current. For example, the addition of 2 equiv. of TFE results in an increase in the peak current from 107 to 148 μ A. The addition of 1 equiv. of MeOTs caused a further increase from 148 to 164 μ A. It was also observed that addition of MeOTs alone was not capable of stopping the parent-child reactions, as an increase in the peak current of the dissociative wave is observed with the addition of acetanilide to a cell containing **1** and a large excess of MeOTs. It would seem that both the anions generated from reduction of **1** are participating in some form of parent-child reaction, therefore it is necessary to add both an acid and a nucleophile trapping agent to observe the maximum peak current.

The voltammetry responds differently to the addition of each reagent. Upon initial addition of acid the peak sharpens, especially apparent at higher scan rates, with α values ranging from 0.44 at 0.1 V/s to 0.53 at 1.0 V/s and then down to 0.37 at 10.0 V/s. The E_p continues to shift negatively as in the absence of acid by 74 mV/decade. The dissociative wave sharpens even further with the addition of MeOTs, most noticeably at the foot of the wave. This is carried over to the values of α , ranging from 0.50 to 0.52 to 0.37 at 0.1, 1.0, and 10.0 V/s, respectively. The addition of both reagents to the cell eliminates the shoulder on the tail





of the dissociative wave and no reduction waves are observed following it prior to the reduction of MeOTs occurring around -2.1 V vs. SCE. This is evidence that it has stopped any parent-child reactions and any products from the reduction that have been trapped are not electroactive in the potential window investigated. The large oxidation near 0 V vs. SCE also disappears, though it remains present in the voltammetry of 1 until MeOTs is added, again confirming its assignment as the oxidation of **3**.

Analysis of the data obtained from voltammograms performed in the presence of both acid and a nucleophile trapping agent allows an important conclusion concerning the mechanism of reduction to be drawn. The values for the peak width, peak current, and the shift in the peak potential are all similar to an electrochemically reversible process (i.e., the reduction of nitrobenzene) suggesting that the bond cleavage, and not the ET, is the rate-determining step. This implies that the ET reduction is occurring by a stepwise dissociative mechanism.

CPE experiments carried out in the absence of both acid and MeOTs required only 1.1 electron equiv., this value being the average obtained over several experiments. CVs taken before and after complete electrolysis are shown in Fig. 1a. Following complete reduction, the dissociative wave has completely disappeared while a small irreversible wave at more negative potentials is present. Scanning anodically, it was found that the peak attributed to the oxidation of 3significantly increased. The cell solution was acidified and MeOTs was added following the electrolysis to aid in product isolation. The majority of the DMF and TFE were removed in vacuo with mild heating (60 °C). The residue was then subjected to column chromatography. Analysis of the fractions obtained by GC and GC-MS indicated the products summarized in Scheme 3. The major products of the reduction, methyl phenyl sulfide (5), benzyl alcohol (6), and diScheme 4. Parent-child reactions involved in the ET reduction of 1.



phenyl disulfide (7), could be identified using GC by comparison with authentic samples. Benzyl phenyl sulfide (8), a minor product, could also be identified by GC comparison. The identities of these products were further confirmed by mass spectrometry. The identities of the other minor products of reduction, benzylbenzenesulfinate (9), *n*-butyl phenyl sulfide (10), and benzyl p-toluenesulfonate (11), are based on their mass spectra. There were some minor products present that could not be conclusively identified by their mass spectra. Compounds 6-9 are products derived from parentchild processes. The remaining products are attributed to secondary reactions involving products of the reduction (3) and 4) with the solvent, electrolyte, or MeOTs. Because of the significance of these secondary reactions, a similar electrolysis was carried out, only switching to acetonitrile (MeCN) as the solvent, which was then worked up as previously described. GC-MS analysis revealed that switching the electrolysis solvent did not simplify the product mixture, and that products produced from reaction with MeCN were also present.

Based on the products observed in the DMF electrolysis, the reactions shown in Scheme 4 have been postulated for the parent-child processes. The first reaction is a nucleophilic attack at the sulfur atom of 1 by 3 to give diphenyl disulfide (7) and 4. The reaction is believed to be occurring, but is in essence inconsequential as 4 is produced by direct ET to 1. Also, at the potential at which the electrolysis is performed, any 7 formed by this reaction will be reduced to give 2 equiv. of 3. This reaction will not affect either the products observed or the charge required for complete electrolysis. The second reaction involves attack at the benzyl carbon of 1 by 3 to give the benzenesulfenate anion and benzyl phenyl sulfide (8). This reaction accounts for the observance of 8 as a product from electrolysis and accounts for the lower charge consumption, as the reduction potential of 8 is negative of the electrode potential during electrolysis. The final parent-child reaction is the deprotonation of the benzyl carbon of 1 to give benzyl alcohol (6), benzaldehyde (13), and 3. Benzaldehyde was observed as a minor product in the CPE experiments carried out in MeCN. The reduction potential of 13 is very close to that of 1 with $E_{13}^{\circ} = -1.85$ V vs. SCE, and it is suggested that the shoulder on the dissociative wave is due to the reduction of 13 (Fig 1*a*). For

Scheme 5. Reactions accounting for the formation of 9.



these reasons it is suspected that 13 will be reduced to its radical anion during the electrolysis of 1. Reduction of 13 in aprotic solvent leads to the formation of 1,2-diphenylethane-1,2-diol (20-25); however, this compound was not observed as a product of our experiments. As the presence of acid is required to observe the full peak current of the dissociative wave of 1, there must be a parent-child reaction involving 4 and 1. Also, reaction between 4 and 1 to give 13 will result in a net decrease in the charge required for complete electrolysis, even if 13 is reduced to its radical anion. The products that were not conclusively identified were consistent with products from reactions between 3 and 13 and could account for the lack of products serving as evidence of the presence of 13. On these grounds, we propose the reaction shown in Scheme 4 as the most likely reaction between 1 and 4.

The formation of benzyl benzenesulfinate (9) cannot be directly accounted for through a parent-child reaction. However, in the reaction leading to 8 the benzenesulfenate anion (12) is generated. A possible reaction of this anion with 1 is illustrated in Scheme 5. Attack at the sulfur atom of 1 by 12 generates phenyl benzenethiosulfinate (14), while releasing 4. A subsequent reaction between 4 and 14 could lead to the formation of 9. Compound 14 could also be generated from attack of 12 on 7 with the release of 3. The other primary process available to 14 would be ET reduction, which would lead to the generation of 12 and 3.

When the reduction is performed in the presence of both MeOTs and acetanilide, a smooth conversion to phenyl methyl sulfide and benzyl alcohol by two-electron reduction is observed. It can be seen in Fig. 1b that no electroactive reagents remain following complete reduction of 1. Both HPLC and GC results confirm quantitative formation of phenyl methyl sulfide (5). GC was used to determine the concentration of benzyl alcohol produced under these conditions, though it was difficult to achieve consistent results, even for the standards used for calibration. GC calibration indicates that 76% of the maximum amount of benzyl alcohol is recovered when the reduction is carried out with acid and MeOTs. These results were consistent with quantitative formation of benzyl alcohol given the error associated with these measurements. Considering that 5 is formed quantitatively and the two-electron stoichiometry for the complete reduction, it is assumed that a less than quantitative return of benzyl alcohol is primarily due to loss during the work-up.

Fig. 2. Representative CVs of 2 in 0.1 mol/L TBAP–DMF at 0.1 V/s: (a) 2 (2.4 mmol/L) before (solid line) and after (dashed line) introduction of 6.0 C of charge into the cell; (b) 2 (2.3 mmol/L) in the presence of acetanilide (40 mmol/L) before (solid line) and after (dashed line) introduction of 11.2 C of charge into the cell and following the subsequent addition of 2.7 mmol/L MeOTs (dotted line).



Analysis of the CV and CPE experimental data leads to the conclusion that the ET reduction of 1 occurs via a stepwise dissociative mechanism and the intermediate radical anion cleaves at the S—O bond.

ET reduction of tert-butyl benzenesulfenate ester (2)

The CV experiments of 2 were performed in 0.1 mol/L TBAP in DMF and the relevant voltammetric data are listed in Table 1 for comparison to the CV data obtained for compound 1. A representative CV of 2 in 0.1 mol/L TBAP-DMF solution is shown in Fig. 2. A narrow, irreversible wave is observed at -2.28 V vs. SCE at 0.1 V/s. A negative shifting of the E_{p} with increasing scan rate is observed at a rate of 103 mV/decade. The peak width increases with increasing scan rate leading to decreasing values of the transfer coefficient. The α values at 0.1, 1.0, and 10.0 V/s are 0.58, 0.50, and 0.37, respectively. These data are in accord with the heterogeneous ET occurring by a stepwise dissociative mechanism, although the shifting of the $E_{\rm p}$ is higher than generally observed for systems proceeding by a stepwise mechanism. The dissociative wave is the only peak present on the cathodic scan, and reversing to the anodic scan reveals only small oxidation waves, starting at -0.4 V

Scheme 6. Mechanism for the ET reduction of 2.



vs. SCE through to the largest oxidation wave occurring at 0.45 V vs. SCE at 0.2 V/s. The origin of these oxidations will be discussed in the context of the electrolysis experiments. It is sufficient at this point to note that unlike the voltammograms for 1, only a small oxidation is present near 0 V vs. SCE. This is an indication that 3 is being produced only in a limited quantity, and the addition of nucleophile traps is deemed unnecessary when studying the electrochemistry of 2. In comparison, for the reduction of 1 a large oxidation wave due to 3 is observed indicating a significant amount of 3 is produced, leading to the conclusion that the radical anion dissociates by S-O cleavage. Limited production of 3 is an indication that S—O bond cleavage is not occurring appreciably and that instead the radical anion of 2 dissociates by breaking the C-O bond as illustrated in Scheme 6. In this scheme, compound 2 is initially reduced by an ET to its radical anion, which then fragments in a separate step. The C-O bond is cleaved in the fragmentation step resulting in the formation of benzenesulfenate anion (12) and the *tert*-butyl radical. The standard reduction potential of this radical is estimated to be -1.54 V vs. SCE (18), which is positive of the E_p of **2**, therefore a heterogeneous ET can reduce this radical to give the *tert*-butyl anion (15).

The addition of a weak, nonnucleophilic acid, such as acetanilide or TFE, causes a significant increase in the peak current. The peak current values, corrected for both concentration and scan rate are 147 µA without acid and 170 µA with acid for a 2 mmol/L solution. Again, some parent-child interaction is responsible for a lower observed peak current in the absence of a reagent to trap the reactive species. The peak not only increased in current, but became narrower, which was especially apparent at higher scan rates. This is demonstrated in the value of the transfer coefficient, ranging from 0.55 to 0.50 and 0.43 at scan rates of 0.1, 1.0, and 10.0 V/s, respectively. Also, the observed shift in the E_p with increasing scan rate decreased from 103 to 72 mV/decade, a value that is more consistent with ET by a stepwise dissociative mechanism. The addition of acid did not dramatically affect the oxidation waves observed in the absence of acid, as it appears that the products responsible for these oxidation peaks are produced in the same quantity in the presence and absence of acid.

To confirm that C—O bond cleavage was occurring in the ET reduction of **2**, CPE experiments were necessary. Performing CPE in the absence of acid required only 1.1 electron equiv. for the complete reduction of **2**. This

Scheme 7. Parent–child reactions involved in the ET reduction of 2.



demonstrates that the parent-child process is highly effective when reduction is carried out on the electrolysis scale. Figure 2a shows CVs of **2** taken before and after the electrolysis. It can be seen that following electrolysis there are no products that are electroactive at negative potentials. However, anodic scans reveal that a large oxidation peak is present at 0.45 V vs. SCE at 0.2 V/s. Small peaks occurring at slightly more negative potentials are also present. Electrolysis performed with a large excess of acetanilide present require 1.96 F/mol (i.e., 2 electron equiv.) for complete reduction indicating that only acid is necessary to effectively suppress any parent-child reactions. Figure 2b shows the before and after CVs from the CPE of 2 with acid and it is seen that again no reducible products are observed and the large oxidation at 0.45 V vs. SCE seen in the voltammetry following CPE without acid is present. There is a large peak just negative of this oxidation, which is due to the oxidation of the acetanilide anion. Figure 2b shows that the addition of MeOTs following electrolysis will remove the oxidation peak of the acetanilide anion along with the smaller oxidation waves also present. The large wave at 0.45 V remains unaffected by the addition of MeOTs. Washing of the cell contents with an organic solvent and water proved inadequate in identifying the products of reduction as essentially no products could be detected in the organic residue by GC or ¹H NMR spectroscopy. In place of typical product analysis, it was decided to further analyze the large oxidation wave present in the CVs of the products of electrolysis.

Given that little to no **3** was observed in the CVs of **2**, C—O bond cleavage is believed to be occurring as shown in Scheme 6. Based on the anions formed from this reduction, the reactions illustrated in Scheme 7 are the proposed parent-child reactions believed to be occurring. The first reaction involves removal of a proton from the terminal methyl groups of **2**. The base involved in this reaction could be the *tert*-butyl anion or more likely the basic species generated from proton abstraction by the *tert*-butyl anion. Deprotonation of **2** generates isobutylene and benzenesulfenate anion (**12**). Therefore, the same product is observed in the voltammetry whether formed from direct reduction or from deprotonation of **2**. This accounts for the observance of the same oxidation wave following the electrolysis of **2** with or without acid.

The second possible parent-child reaction involves nucleophilic attack of 2 by 12. This process is identical to that proposed in the formation of 9 from the ET reduction of 1, as previously shown. Again, phenyl thiobenzenesulfinate (14) is produced only now with the *tert*-butoxide anion as



Scheme 8.





Table 2. Bond lengths (Å) calculated for the equilibrium conformers of 1 and 2 and their respective radical anions.

Bond	1 (Å)	1 (Å)	2 (Å)	2 (Å)
C—S	1.764	1.734	1.765	1.787
S—O	1.702	1.776	1.702	1.668
0—C	1.423	1.384	1.441	1.439

the leaving group. The presence of *tert*-butoxide is believed to account for the small oxidation wave at -0.4 V vs. SCE in the CVs of **2**. Any **14** produced will likely be reduced to return to **12** and **3** (Scheme 5) and this reaction accounts for the oxidation wave at 0 V vs. SCE attributed to the oxidation of **3**.

However, the primary product from CPE of 2 in the presence and absence of acid is responsible for the oxidation peak at 0.45 V vs. SCE. We attribute this peak to the oxidation of benzenesulfinate (16), which is formed from the oxidation of 12 (Scheme 8). Evidence in favour of this assignment comes from the addition of sodium benzenesulfinate to the cell solution following CPE of 2. The peak at 0.45 V increased in peak current and no new peaks were observed, while the $E_{\rm p}$ remained relatively constant indicating that the peak was likely due to the oxidation of benzenesulfinate. Independent CV experiments were performed that confirmed that the $E_{\rm p}$ of the sodium benzenesulfinate coincided with that of the oxidation wave observed in the electroysis of 2. By varying the concentration of the sodium benzensulfinate the current response was calibrated and the concentration of 16 formed in the electrolysis was determined. As much as 75% of 2 was converted to 16 in the electrolysis performed without acid, and 16 was present in 96% of the starting concentration of 2 for CPE experiments performed with acid. How the conversion of 12 to 16 occurs is not completely understood. Previous studies of the electrolysis of phenyl benzenethiosulfinate also reported a similar oxidation wave that was attributed to 16 (26). In this study it was hypothesized that a disproportionation reaction between two molecules of 12 was occurring to give 3 and 16. While it is possible that this process occurs, the relative peak currents of the oxidation peaks due to 3 and 16 indicate that it is not the primary process leading to the generation of 16. It is difficult to assign a particular pathway for the oxidation of benzenesulfenate. Oxidation by perchlorate is unfavourable and oxidation by the solvent requires a significant amount of residual water to be present. It should be recognized that the E_p of an irreversible wave is not the most reliable means of identifying an unknown present in solution and that the wave could be due to the oxidation of benzenesulfenate and that the oxidation peaks of benzenesulfenate and benzenesulfinate simply coincide. Since benzenesulfenate is a highly unstable species, it was not possible to obtain an authentic sample to check this assertion.

DFT calculations of the SOMOs

It is interesting to compare the differences in the ET reactions of 1 and 2 that result as a difference in the O group. The most intriguing result of changing the ester moiety is the resulting change in the mode of fragmentation of the radical anions. The factors that result in the difference in cleavage reactions are not obvious. The same anionic fragment, either phenyl thiolate (11) or benzenesulfinate (22), would result from S—O and C—O cleavage of each compound, so it is not related to a thermodynamic advantage imparted by the stability of the anionic product. In both cases the carbon radical formed from C—O cleavage would be relatively stable; estimates of the reduction potentials of the benzyl radical and the *tert*-butyl radical have them near -1.34 and -1.54 V vs. SCE (18), respectively.

The difference seems to be related to differences in the electronic configuration of the radical anion intermediate for each of 1 and 2. The SOMO for each of these compounds was determined by performing PM3 calculations to determine the equilibrium conformer of the radical anion and then density functional theory calculations at the BLYP-3//6-31** level were performed to arrive at the SOMO for each compound. The results of these computations are depicted in Fig. 3. The SOMO of the radical anion of 1 was largely associated with the S—O bond while the SOMO of the radical anion of 2 was largely delocalized over the phenyl ring and S atom. The respective bond lengths of the starting compound and its radical anion determined by PM3 calculations are given in Table 2. The ET to 1 causes significant lengthening of the S—O bond, while the S—O bond of 2 shortens upon ET. For 1 the majority of the additional charge is associated with the S—O bond and S—O cleavage is the result. For 2 the charge is delocalized onto the phenyl ring with only a limited effect on the S-O and C-O bonds, and

cleavage follows the most thermodynamically favourable pathway. Gregory and Jenks (17) have performed calculations for the homolytic cleavage of disulfides, peroxides, and sulfenate esters. While it was found that S—S and O—O cleavage were the most energetically viable pathways for disulfides and peroxides, the results indicated that fissure at the C—O bond is the most thermodynamically favourable mode of cleavage for a sulfenate ester. Our experimental results indicate that such an advantage is present in the radical anion of $\mathbf{2}$ as well.

Regioselective bond cleavages were observed by Houmam et al. (27) in their study of the ET reduction of benzyl thiocyanates, where differences in the mode of cleavage were observed for benzylthiocyanate and 4-nitrobenzylthiocyanate. The differences in this case were related to the radical anion intermediate, with benzylthiocyanate forming a σ^* type radical anion akin to compound 1 and nitrobenzylthiocyanate forming a π^* radical anion intermediate as was observed for 2. In this case, the difference in the electron distribution of the radical anions of 1 and 2 must be related to the nature of the ester functionality as opposed to the aromatic moiety. The electron-donating capacity of the tert-butyl group increases the electron density on the O atom shifting the SOMO onto the aromatic ring. The benzyl group has the opposite effect, decreasing the electron density at the O atom and drawing the SOMO onto the S-O bond.

Conclusions

The ET reduction of benzyl benzenesulfenate ester (1) and tert-butyl benzenesulfenate ester (2) has been investigated. In each case, ET reduction generates a radical anion intermediate that subsequently undergoes bond cleavage. The bond that cleaves upon reduction, however, differs for the two compounds. ET reduction of 1 leads to S-O bond cleavage to give phenylthiolate and phenylmethoxide in an overall two-electron process. Complicating secondary reactions are effectively suppressed by addition of appropriate trapping reagents. The ET reduction of 2 leads to C-O cleavage of the radical anion. In the presence of acid the reduction proceeds to quantitatively generate benzenesulfenate. The difference in the mode of cleavage for these two radical anions is most likely related to the electron distribution in the radical anion. The additional charge on the radical anion of 1 is largely associated with the S-O bond, leading to significant S-O bond stretching upon ET and ultimately, bond fragmentation. The additional electron on the radical anion of 2 is largely associated with the phenyl ring and S atom so the dissociation of the radical anion follows the most thermodynamically favourable pathway, which in this case is C—O cleavage.

Experimental

General

The NMR spectra were obtained using a Varian Mercury 400 MHz spectrometer using the solvent peak (CDCl₃, 7.28 ppm) as the reference. ¹H and ¹³C NMR spectra were recorded at 400.1 and 100.6 MHz, respectively. Mass spectra were performed using a MAT 8200 Finigan high-resolution mass spectrometer. GC was performed using an Agilent

technologies GC 6890N gas chromatograph. HPLC was carried out using a Waters 600 controller and Waters Delta 600 pump, a Waters 2487 dual λ absorbance detector all interfaced to a PC using Millenium software, and a Hamilton PRP-1 column.

Calculations were performed on a PC using the SPARTAN program, which performed the PM3 and DFT calculations. The method for the calculations of the SOMOs of the sulfenate ester radical anions involved a geometry optimization of the structure using semiempirical PM3 calculations followed by a single-point energy DFT calculation using the B3LYP//6-31G** basis set.

Electrochemical apparatus and procedures

Cyclic voltammetry was performed using either a PAR 283 or PAR 263 model EG & G potentiostat interfaced to a personal computer using the M270 DOS-based software. A standard three electrode arrangement, with working, counter, and reference electrodes, was employed. The cell was maintained at a constant temperature of 25 °C with continuous purging using high purity Ar gas throughout the experiment. The working electrode was a 3 mm diameter glassy carbon rod (Tokai) sealed in a glass tube with epoxy resin. The working electrode was cleaned prior to use by polishing with 0.25 µm diamond paste, rinsing with 2-propanol, and placed in a sonicator in 2-propanol for 10 min. Electrochemical activation of the electrode was performed by cycling several times between 0 and -2.7 V at 0.2 V/s in the background solution. The counter electrode was a platinum plate, which was symmetrically placed under the working electrode. The reference electrode consisted of a silver wire immersed in a 0.1 mol/L solution of the electrolyte in the appropriate solvent contained in a narrow glass tube with a fine sintered glass tip. The reference potential was calibrated following each experiment using the ferrocene/ferrocenium couple whose standard potential under our conditions was 0.464 V vs. SCE. All reported potentials are referenced to SCE.

The CPE experiments were carried out using the same cell set up protocol and a similar cell arrangement. In controlled potential electrolysis, there is the inclusion of a second working electrode, which is a 2.5 cm (dia.) \times 0.8 cm (width) glassy carbon disk, custom fit into a Teflon jacket that attaches to a Radiometer ED-101 rotating disk assembly. A radiometer CTV101 speed control unit was used to regulate the velocity of the rotating disk electrode (RDE), which was maintained at 4500 rpm for these experiments.

Materials

Dry solvents were obtained from an Innovative Technology SPS-400-5 solvent purification system and were stored a maximum of 5 days under an N₂ atmosphere. Tetrabutylammonium perchlorate (Aldrich, Fluka) was purified by multiple recrystallizations from 95% EtOH and the crystals subsequently vacuum-dried at 60 °C overnight. The recrystallized and dried electrolyte was then stored in a dehumidifying cabinet. Benzyl alcohol, benzaldehyde, diphenyl disulfide, thioanisole, benzenethiol, sulfuryl chloride, and *m*-chloroperbenzoic acid were purchased from Aldrich and purified by standard procedures when necessary.

Benzyl benzenesulfenate ester (1)

Compound 1 was prepared by the reaction of lithium phenylmethoxide and benzenesulfenyl chloride as previously reported (28). The crude product was a deep yellow oil, which was purified by vacuum distillation at 100 °C and >0.5 mmHg (1 mmHg = 133.322 4 Pa) using a Kugelrohr apparatus to give a pale yellow oil. ¹H NMR (CDCl₃) δ : 7.40–7.43 (m, 2H), 7.26–7.32 (m, 4H), 7.17–7.22 (m, 2H), 7.09–7.15 (m, 2H), 4.70 (s, 2H). ¹³C NMR (CDCl₃) δ : 140.13, 136.92, 128.96, 128.39, 127.32, 127.02, 126.69, 124.32, 79.50.

tert-Butyl benzenesulfenate ester (2)

Compound **2** was prepared by reaction of *tert*-butyl alcohol and benzenesulfenyl chloride in the presence of pyridine as previously reported (29). Purification was performed by column chromatography using hexanes – ethyl acetate (4:1) as the eluent to give a clear, colourless oil. ¹H NMR (CDCl₃) δ : 7.66–7.70 (m, 2H), 7.49–7.53 (m, 3H), 1.56 (s, 9H). ¹³C NMR (CDCl₃) δ : 146.46, 131.54, 128.90, 124.86, 82.87, 29.87.

Benzyl phenyl sulfide (8)

Compound **8** was prepared by the addition of a solution of benzylbromide (5.9 mmol) in ~25 mL CH₂Cl₂ to a flask containing benzenethiol (5.8 mmol) and pyridine (6.2 mmol) dissolved in 25 mL of CH₂Cl₂. The reaction mixture was washed with aq. K₂CO₃ solution, which was then washed with CH₂Cl₂. The organic extracts were combined and washed three times with H₂O and dried over anhydr. Na₂SO₄. The crude product was purified by column chromatography with hexanes – ethyl acetate (10:1) as the eluent. ¹H NMR (CDCl₃) δ : 7.21–7.37 (m, 10H), 4.17 (s, 2H). ¹³C NMR (CDCl₃) δ : 137.33, 136.28, 129.64, 128.73, 128.39, 127.08, 127.02, 126.21, 38.88.

Phenyl benzenethiosulfinate (14)

Compound 14 was prepared by the oxidation of diphenyl disulfide with *m*-chloroperbenzoic acid according to accepted literature methods (30–32). Column chromatography was employed for the purification using hexanes – ethyl acetate (10:1) as the eluent. ¹H NMR (CDCl₃) δ : 7.64–7.68 (m, 2H), 7.47–7.56 (m, 5H), 7.41–7.46 (m, 1H), 7.34–7.40 (m, 2H). ¹³C NMR (CDCl₃) δ : 143.96, 135.33, 131.50, 130.26, 129.24, 128.89, 127.52, 124.29.

Identification of products from the CPE experiments of 1

Product mixtures and authentic samples were subjected to analysis by GC using a 15 m HP-5 column. The method used to obtain the gas chromatograms is as follows: the initial temperature is 80 °C and upon initiation the temperature is increased to 280 °C at a rate of 15°/min and held at 280 °C for 5 min. Following partial separation of the products into two major fractions by column chromatography, the fractions of the product mixture were analyzed by GC– MS. The method for the GC of these analyses is as follows: the temperature is initially set at 60 °C and held for 3 min. The temperature is then ramped to 300 °C by 15°/min.

Methyl phenyl sulfide (5)

The presence of **5** in the product mixtures could be inferred from the observation of a peak in the GC chromatogram of the product mixture with the same retention time as an authentic sample of **5** purchased from Aldrich. GC– MS of this peak had the following major peaks: 124 (100%) M^+ , 109 (47%) M^+ – CH₃, 91 (57%) M^+ – SH, 78 (65%) M^+ – SCH₂.

Benzyl alcohol (6)

The presence of **6** in the product mixtures was determined from the observation of a peak in the GC chromatograms of the products with the same retention time as an authentic sample of **6** purchased from Aldrich. The corresponding peak in the GC–MS had the following mass spectrum characteristics: 108 (100%) M⁺, 91 (25%) M⁺ – OH, 79 (75%) M⁺ – CHO.

Diphenyl disulfide (7)

The presence of **7** in the product mixtures was determined from the observation of a peak in the GC chromatograms of the products with the same retention time as an authentic sample of **7** purchased from Aldrich. The corresponding peak in the GC–MS had the following mass spectrum characteristics: 218 (100%) M⁺, 185 (28%) M⁺ – HS, 154 (30%) M⁺ – H₂S₂, 140 (10%) M⁺ – C₆H₆, 109 (99%) M⁺ – SC₆H₆, 65 (42%), 109 – CS.

Benzyl phenyl sulfide (8)

The presence of **8** in the product mixtures was determined from the observation of a peak in the GC chromatograms of the products with the same retention time as an authentic sample of **8** prepared as previously described. The corresponding peak in the GC–MS had the following mass spectrum characteristics: 200 (83%) M⁺, 109 (19%) M⁺ – C₇H₇, 91 (100%) M⁺ – C₆H₅S, 65 (45%), 109 – CS.

Benzyl benzenesulfinate (9)

The presence of **9** in the product mixtures was determined from the analysis of the GC–MS of the product mixture. The peak assigned to this product had the following mass spectrum characteristics: 232 (1%) M⁺, 167 (6%) M⁺ – C₅H₅, 153 (2%) 167 – CH₂, 125 (6%) M⁺ – C₇H₇O, 91 (100%) M⁺ – C₆H₅O₂S, 77 (23%) 91 – CH₂, 65 (9%) M⁺ – C₈H₈O₂S.

n-Butyl phenyl sulfide (10)

The presence of **10** in the product mixtures was determined from the analysis of the GC–MS of the product mixture. The peak assigned to this product had the following mass spectrum characteristics: 166 (77%) M⁺, 152 (4%) M⁺ – CH₂, 123 (100%) M⁺ – C₃H₇, 109 (49%) M⁺ – C₄H₉, 91 (5%) M⁺ – C₃H₇S, 77 (11%) M⁺ – SC₄H₉, 65 (12%), 109 – CS.

Benzyl p-toluenesulfonate (11)

The presence of **11** in the product mixtures was determined from the analysis of the GC–MS of the product mixture. The peak assigned to this product had the following mass spectrum characteristics: 262 (12%) M⁺, 244 (3%) M⁺ – H₂O, 186 (3%) M⁺ – C₆H₅, 107 (100%) M⁺ – C₇H₇O₂S, 91 (12%) M⁺ – C₇H₇O₃S, 79 (52%), 107 – CO.

Benzaldehyde (13)

The presence of **13** in the product mixtures from CPE experiments performed in MeCN was determined from the observation of a peak in the GC chromatograms of the products with the same retention time as an authentic sample of **13** purchased from Aldrich. The corresponding peak in the GC–MS had the following mass spectrum characteristics: 108 (100%) M⁺, 91 (26%) M⁺ – OH, 79 (73%) M⁺ – CHO.

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